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Thermal and temporal stability of V/Sc multilayer mirror for the soft X-ray water window region

QIANG YI[2], QIUSHI HUANG[1]*, JINSHUAI ZHANG[1], XIANGMEI WANG[1], RUNZE QI[1], ZHONG ZHANG[1], ,RONGKUN XU[2], TAIPING PENG[2], PHILIPPE JONNARD[3,4], ANGELO GIGLIA[5] , ZHANSHANWANG[1]*

[1]*Key Laboratory of Advanced Micro-Structured Materials MOE, Institute of Precision Optical Engineering, School of Physics Science and Engineering, Tongji University, Shanghai 200092, China*

[2]*Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang 621900, China*

[3]*Sorbonne Universités, UPMC Univ Paris 06, Laboratoire de Chimie Physique – Matière et Rayonnement, 11 rue Pierre et Marie Curie, F-75231 Paris cedex 05, France*

[4]*CNRS UMR 7614, Laboratoire de Chimie Physique – Matière et Rayonnement, 11 rue Pierre et Marie Curie, F-75231 Paris cedex 05, France*

[5]*CNR Istituto Officina Materiali 34149 Trieste, Italy*

**huangqs@tongji.edu.cn*

**wangzs@tongji.edu.cn*

Abstract

V/Sc multilayer has been developed as a promising candidate for the water window region working near both the Sc-L edge (3.11 nm) and the V-L edge (~~λ=~~2.42 nm). To meet the application requirements, its thermal and temporal stability ~~of it~~ are studied. A series of V/Sc multilayers with a d-spacing ranging from 1.59 to 1.62 nm and a number of bilayers of 100 and 400 was fabricated. Different samples were annealed at temperatures from 100 to 300˚C. Grazing incidence X-ray reflectivity and soft X-ray reflectivity (SXR) measurements showed that the multilayer structure and reflectivity remain mostly unchanged at 100˚C. An obvious deterioration started at 200˚C, while the SXR reflectivity drops close to zero at 250˚C. The multilayer structure completely broke down at 300˚C. Both ~~the~~ X-ray diffraction and transmission electron microscopy measurements demonstrated a severe crystallization occurring at 250˚C ~~which can be mainly identified as Sc(002) and V(110)~~. Energy dispersive X-ray spectroscopy measurements have further confirmed a significant elemental mixture occurring after 250˚C annealing. The severe intermixing and polycrystallization resulted in the degradation of the multilayer structure. On the other hand, the V/Sc multilayer is relatively stable after half year storage in air environment showing a slight decrease of ~~SXR~~ reflectivity from 18.4% to 16.5%.

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1. Introduction

Soft X-ray imaging at the water window wavelength region (λ=2.3 ~~nm~~-4.4 nm) is of great importance for biology science due to the natural imaging contrast between carbon and water [13]. Spatial resolution and exposure time are the two critical parameters to evaluate the performance of a microscope. Presently a high spatial resolution of 10 nm [4,5] has been demonstrated while the exposure time and the system efficiency still needs to be improved particularly for the compact microscopes based on the plasma source and high harmonic generation (HHG) source [6]. On the other hand, the rapid advancement of free-electron laser (FEL) facilities with the wavelength ranging into water window region is also motivating the development of the related microscopy techniques [7]. The performance of the microscope is affected by each optical component, like the condenser, objective mirror, polarizer, and so on [5,8,9]. Multilayer mirrors are widely used in the water window microscopes. They have the advantages of providing relatively high collection efficiency, with large numerical aperture and well-defined spectral selectivity.

Due to the short wavelengths of the water window region, the near normal incidence multilayers require a d-spacing of less than 2 nm and each layer thickness is below 1 nm. This imposes a big challenge to the development of related multilayer optics. Sc-, Ti-, and V-based multilayers are usually selected in the water window range given to their absorption edges at λ=3.109 nm, 2.730 nm, and 2.420 nm, respectively [4]. Among which, Cr/Sc multilayer is the most widely studied and used near the Sc L-edge [1012]. The highest reflectance of Cr/Sc achieved was 32.1% at λ=3.11 nm, in which the structure is optimized by the introduction of diffusion barrier layers of B_4C [12]. Despite the improved experimental reflectance, this value is still much lower than the theoretical prediction of around 60%. To further enhance the reflectance, Loch et al.

proposed a new material combination of V/Sc. It has the same theoretical reflectance as Cr/Sc at near the Sc-L edge with even a little higher single-shot damage threshold in theory [13]. Moreover, the same V/Sc multilayer can also work at near V-L edge at grazing incidence which is a unique advantage for application. Inspired by this result, we have recently studied this multilayer experimentally which showed smaller interface widths than the Cr/Sc multilayer with no interface engineering methods applied. A high reflectance of 18.4% was measured at 3.129 nm under a near normal incidence of 11º based on the first experiment on V/Sc [14], demonstrating a new and competitive candidate for the multilayer mirror working in the water window region. The detailed results can be found in reference [14].

Despite the promising optical performance, stability is another critical factor for the application of multilayer mirrors with harsh working environment, e.g. under high irradiation power [15,16]. Thermal stability of the conventional Cr/Sc multilayer has been widely studied. Majkova et al [15] has found that Cr/Sc multilayer shows a reduction of 1st Bragg peak intensity by 25% after annealing for 33 h under 280˚C and a structure collapse after annealing under 650˚C for 3 h. Eriksson et al. have also observed a continuous degradation starting at 100˚C and a complete destruction at 510˚C of the pure Cr/Sc multilayer [16]. Prasciolu et al. have found that Cr/Sc multilayer shows a reduction of 1st Bragg peak intensity by 15% after annealing at 150°C for 1 h and a structure collapse after annealing at 450°C for 1 h [7]. The small difference of thermal stability was attributed to the different layer thickness and fabrication methods. The thermal stability of Cr/Sc can be enhanced by introducing nitrogen in the working gas or by using B_4C as barrier layers. For instance, the nitridated Cr/Sc multilayers display an improved structural quality upon annealing to 250˚C and a final breakdown above 510˚C [16]. Prasciolu et al. have reported that the thermal stability of Sc/B_4C/Cr multilayers is much improved than Sc/Cr and the structure collapsed after annealing for over 12 h under 600˚C [7].

The thermal and temporal stabilities of the new V/Sc multilayer candidate were not reported before. In order to use the V/Sc multilayer in various applications, the layer structure and reflectivity changes of V/Sc multilayers under elevated temperatures and long-term storage are investigated in this paper. A moderate thermal stability and relatively good temporal stability are found based on the different characterization results. The stability of V/Sc is compared to the one of Cr/Sc and the related physical mechanisms for the changes are discussed.

2. Experiments

The multilayers were deposited by direct current magnetron sputtering technique. The base pressure used in the deposition chamber is 6.0×10^{-5} Pa. High purity argon (99.999%) is used as the sputtering gas with a sputtering pressure of 0.13 Pa. The depositions rates of V and Sc were 0.04 nm/s and 0.07 nm/s, respectively. The deposition parameters were designed with a d-spacing of 1.60 nm and a thickness ratio of γ~0.5. Five (after you write “four” samples. But perhaps are you adding a non-anneled sample for comparison purpose. At the moment it is not clear.) samples with 100 bilayers for thermal stability study and a sample with 400 bilayers for temporal stability study were deposited. A B_4C layer was added on the top of all multilayers as capping layer with 2-3 nm thickness to prevent oxidation. It will only induce about 1% (absolute) reduction of the theoretical reflectance of the multilayer [**Erreur ! Signet non défini.**]. The annealing experiments were performed on the four samples with 100 bilayers in a high vacuum environment with a pressure lower than 5×10^{-4} Pa [17]. The four samples were annealed for one hour at 100˚C, 200˚C, 250˚C, and 300˚C, respectively. Each annealing process was conducted with a heating rate of 5˚C/min.

(New paragraph) All multilayers were measured by the grazing incidence X-ray reflectometry (GIXR) at the Cu-Kα emission line (λ=0.154 nm) before and after annealing. The soft X-ray (SXR) reflectivity of the as-deposited and annealed samples was measured using the reflectometer at the Bending magnet for Emission Absorption and Reflectivity (BEAR) beamline at the ELETTRA synchrotron facility. The X-ray diffraction (XRD) scans between 2θ = 30˚ ~ 50˚ were collected to study the crystallization change of the annealed samples. The morphology and internal structure of the multilayer sample with 400 bilayers as-deposited and the sample with 100 bilayers after annealing at 250˚C were further characterized by transmission electron microscopy (TEM). The TEM measurements were performed by using the FEI Tecnai G2 F20 equipment by

Materials Analysis Technology Inc. High resolution bright field images, selected area electron diffraction (SAED) patterns were taken to study the layer structure changes and energy dispersive X-ray spectroscopy (EDX) were used to analyze the elemental distribution.

The V/Sc multilayer with 400 bilayers is further stored in air environment with ~20% humidity at room temperature for 6 months in order to study its temporal stability. The layer structure of the sample was monitored by measuring the GIXR during the storage period. The SXR reflectivity of the sample was measured at the ELETTRA synchrotron both before and after the 6 months storage.

3. Results and discussion

3.1 Thermal stability

3.1.1 GIXR measurements

(there was a mix of present and past tense in this paragraph; I put it at the present tense but after I have seen that the following paragraph is at the past tense) The measured GIXR curves of the four annealed samples are shown in Fig. 1. For the sample annealed at 100˚C as shown in Fig. 1(a), the reflectivity and bandwidth of the 1stand 2nd order Bragg peaks are almost the same as that of the as-deposited one, which indicates a similar periodic multilayer structure. The position of the small oscillation before the 1st Bragg peak slightly shifts that may be caused by the change of the surface B_4C layer or the first few bilayers of V and Sc. For the sample annealed at 200˚C as shown in Fig. 1(b), the 1st Bragg peak reflectivity decreases by a small amount of 15% (relatively) while the 2nd Peak reflectivity drops significantly by 38% (relatively). It is also found that the two Bragg peaks shift slightly to smaller angles, indicating a slight expansion of the d-spacing by 0.02 nm. This means the V/Sc multilayer structure started to change ~~obviously~~ at 200˚C. As the annealing temperature increases to 250˚C, Fig. 1(c), the 1st Bragg peak reflectivity drops dramatically by one order of magnitude and the 2nd Bragg peak cannot be observed. The period expansion is still very small, below 0.02 nm. A small peak appears at 1.5° which can be from the interference effect of a newly formed structure inside the stack. Evidently, the layer interfaces are much deteriorated ~~after 250˚C annealing~~. For the sample annealed at 300˚C, Fig. 1(d), the 1st Bragg peak almost vanishes and a small peak appears at around 1°. The multilayer structure completely breaks down ~~after annealing at 300˚C~~. The detailed measured results and structural parameters of the annealed samples are listed in table 1.

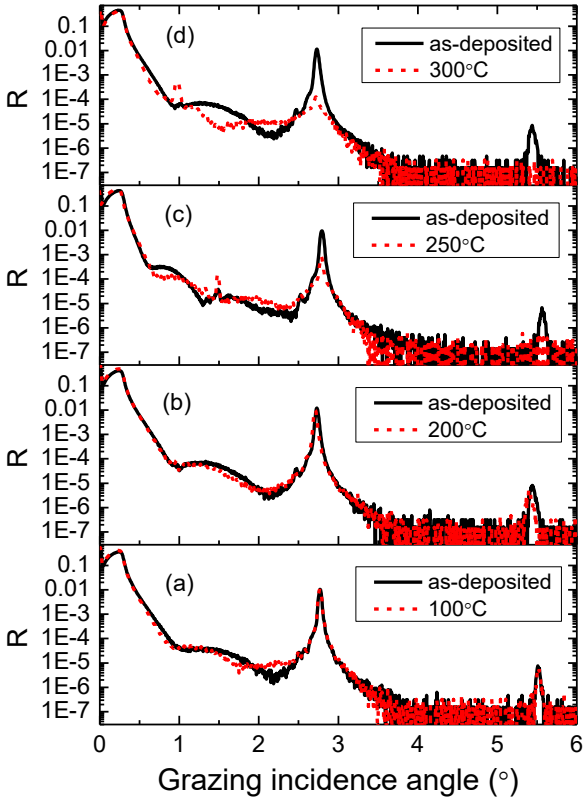

Fig.1. GIXR curves of the samples before and after annealing under different temperatures (a) 100°C, (b) 200°C, (c) 250°C, and (d) 300°C.

Table1. Structural parameters and the GIXR and SXR measurement results of the annealed samples under different temperatures.

Annealing Temperature	As-deposited	100˚C	200˚C	250˚C	300˚C
Bilayers	100	100	100	100	100
1st order reflectivity at 8 keV* (normalized)	1	1	0.845	0.092	0.011
d-spacing before/after annealing	1.60 nm	1.60 nm/1.60nm	1.62nm/1.64nm	1.59nm/1.60nm	1.62 nm/Breakdown
SXR peak wavelength	3.147 nm	3.150 nm	3.155 nm	3.143 nm	___
SXR reflectivity	2.99%	2.91%	2.09%	0.19%	___

*The reflectivity is normalized to the value of the as-deposited value.

3.1.2 XRD measurements

To study the structure changes occurring under annealing, ~~the~~ XRD measurements of the as-deposited and annealed V/Sc multilayers with 100 bilayers were performed and are displayed in Fig. 2. For the as-deposited sample, a broad diffraction peak was observed at about 35.6º which indicated a very weak polycrystallization. This can be mainly identified as the crystalline phase of hexagonal Sc (101). For the sample annealed under 100˚C, the diffraction peak was almost the same as the as-deposited one. As the temperature increased to 200˚C, the peak intensity was slightly enhanced and a new peak seems to appear at the lower angles of around 34~~.0~~º. After annealed at 250˚C, the diffraction peaks were significantly changed. The original broad peak become much narrower and centered at 34.0°, which was identified as hexagonal Sc (002). The

crystallization of Sc (002) was also reported in the Cr/Sc multilayers under annealing [7]. Besides, a new diffraction peak also appeared at around 42.1°, that can be identified as the crystalline phase of cubic V (110). As the annealing temperature further increased to 300˚C, the two diffraction peaks were significantly enhanced while no other peaks appeared. Although a small amount of impurities of oxygen, nitrogen and carbon can exist in the layers as indicated by the EDX measurement in the next section, the crystallization of oxides and carbides were not considered as the content would be low ~~even if existed~~. Assuming that the diffraction peak corresponds to a single phase, it can be calculated by the Scherrer equation [18] that the grain sizes of Sc (002) and V (110) are 5.30 nm and 2.16 nm, respectively, after 250˚C annealing. For the sample annealed at 300˚C, the grain sizes increased to 9.80 nm for Sc (002) and 5.80 nm for V (110), respectively.

(New paragraph) ~~According to the XRD results,~~ The polycrystalline structure of the multilayer starts to change at 200˚C and new phases are forming at 250˚C with relatively large grain size as compared to the layer thicknesses. After 300 ˚C annealing, the crystallization further increased with much larger grain size. This is consistent with the deterioration process of the multilayer observed in the GIXR measurements. As the size of the crystallites are much larger than the single layer thickness of V and Sc (0.8 nm), a severe inter-diffusion probably occurred during the annealing process.

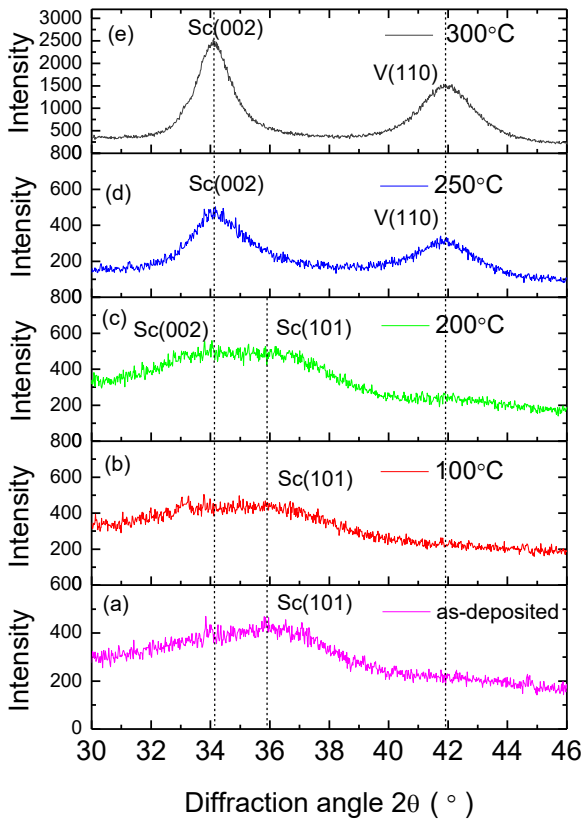

Fig. 2. XRD pattern of V/Sc multilayers under different annealing temperatures.

3.1.3 SXR ~~reflectivity~~ measurements

The SXR ~~reflectivity~~ results of V/Sc multilayers with 100 bilayers are shown in Fig. 3. Given to the small difference of the d-spacings among samples, they were measured under the incidence angle of 13º-11º to make the peak position appearing at around the same wavelength. The peak reflectance of the as-deposited V/Sc multilayer was 3.0% at λ=3.147 nm. After

annealing at 100˚C, the reflectivity was 2.9% at 3.150 nm, which was almost the same as the as-deposited one. The peak reflectivity dropped significantly by 30% (relatively) to 2.1% at 3.155 nm after the sample was annealed at 200˚C. This deterioration was more pronounced than the change ~~of hard X-ray reflectivity~~ shown in the GIXR measurements. It can be explained by the effect from the oxidation and other structural changes of the surface layers that the hard X-ray reflectivity measurement is not very sensitive to. As the sample was annealed under 250˚C, the SXR reflectivity decreased down to 0.2% at 3.143 nm. With the annealing temperature rising up to 300˚C, the reflectance was too low to be measured and is not shown here. The SXR measurement results are also listed in table 1. Both the SXR and the GIXR results have indicated that the layer structure of the V/Sc multilayers started to deteriorate at around 200˚C, and it was mostly destructed at 250˚C. For the Cr/Sc multilayer, the deterioration starts at ~100˚C, while the relative drop of SXR reflectivity is around 30% at 300˚C and the structure breaks down at above 450˚C [7,15,16]. As a comparison, the thermal stability of pure V/Sc multilayer is not as good as Cr/Sc.

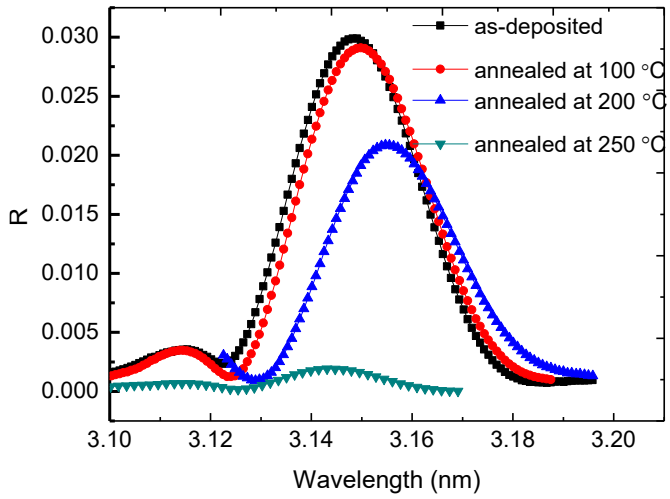

Fig. 3. SXR measurements of V/Sc multilayer as-deposited and annealed at different temperatures.

3.1.4 TEM measurements

The layer morphology and microstructure of the multilayers before and after annealing were further studied by TEM. The cross-sectional images of the as-deposited sample with 400 bilayers and the 250˚C annealed sample with 100 bilayers are shown in Fig. 4. The bottom part of the 400-bilayers stack represents the structure of the 100-bilayers multilayer before annealing. As depicted in Fig. 4, the bright layers are Sc and the dark layers are V. For the as-deposited sample (Fig. 4(a)), the multilayer exhibited a clear periodic layered structure with a d-spacing of about 1.62 nm. The SAED pattern in Fig. 4(b) showed a relatively weak polycrystallization of the layers and the diffraction spots were identified as Sc (101)[14]. This is consistent with the XRD results (Fig. 2(a)). For the sample annealed at 250˚C, the image of the whole multilayer structure is shown in Fig. 4(c). A major part of the layers especially at the middle area of the stack were degraded and barely observed. Only a few layers at the bottom near the substrate and at the top part can still be seen. High resolution images of the middle and surface area of the multilayer are shown in Fig. 4(e) and (f), respectively. In the middle area of the stack (Fig. 4(e)), the layers are heavily crystallized with relatively large grains randomly distributed (is the size of the grains in agreement with the one deduced from the Scherrer formula?), while the ~~layer~~ interfaces completely disappeared. For the surface area (Fig. 4(f)),

a few topmost layers were seen with slight polycrystallization. The crystallization became stronger for the layers located deeper inside the multilayer and the ~~layer~~ interfaces gradually blurred. The bottom layers near the substrate exhibited a similar phenomenon and it was not shown here. The SAED result also showed an enhanced diffraction pattern (Fig. 4(d)), comparing to the as-deposited one, and the main spots were identified as hexagonal Sc (002) and cubic V (110), respectively. The increased crystallization with large grains and newly formed phases is consistent with the XRD result (Fig. 2(d)).

(New paragraph) The ~~energy dispersive X-ray spectroscopy (~~EDX measurements were performed at the cross-section of the two samples as illustrated in Fig. 5. For the as-deposited sample (Fig. 5(a)), periodic oscillations of the relative concentration (what do you call "relative concentration"? I would expect that the sum of V and Sc concentrations should give 100%, which is not the case from what I see on the figure.) of V and Sc were observed, despite the very small d-spacing of 1.59 nm. For the sample after annealing at 250˚C (Fig. 5(b)), no periodic oscillation can be seen. A small amount of oxygen, carbon and nitrogen were also detected in the multilayer while the absolute concentration cannot be determined due to the limited accuracy of EDX. It is clear that the V and Sc atoms significantly mixed at the interfaces after annealed at 250˚C. The increased interdiffusion contributed to the formation of V and Sc nano-grains and these two processes destroyed the original ~~layer~~ interfaces and resulted in the dramatic reduction of the reflectance for the annealed V/Sc multilayers. These processes first occurred at the middle part of the stack which may be caused by the larger interdiffusion of V and Sc atoms from neighboring layers (do you have an idea of the diffusion length to justify such a statement?) and thus an earlier crystallization of the layers, comparing to the surface and bottom part.

The thermal degradation of Cr/Sc multilayers were also caused by the formation of a mixture of Cr and Sc nanocrystallites that broadened the interfaces [16]. Nevertheless, the severe crystallization starts from the temperature of around 450˚C that is at higher temperature than for the V/Sc multilayer. The as-deposited Cr/Sc multilayer also exhibited an amorphous structure while the V/Sc multilayer already shows a polycrystalline structure before annealing. The formation of randomly distributed nano-grains at a lower temperature can be the main reason for the relatively poor thermal stability of V/Sc with respect to Cr/Sc.

It is worth to note that the thermal stability of the multilayer studied here is for pure V/Sc structure with no interface engineering methods applied. Although the thermal stability of V/Sc is a little worse than Cr/Sc, it may be improved by introducing diffusion barrier layers or nitridation, as have been done on the Cr/Sc multilayer. It is very likely that e.g. an atomic-scale B_4C barrier layer can reduce the inter-diffusion of atoms under high temperature annealing, suppress the formation of large crystallites, and result in a better thermal stability [4]. Nevertheless, this will need to be investigated in the future.

Les paramètres requis sont manquants ou erronés.

Fig. 4. (a) TEM image, and (b) SAED pattern of the as-deposited 400-bilayer V/Sc multilayer; TEM image of (c) the whole stack, (e) the middle area and (f) the surface area, and (d) SAED pattern of the 100-bilayer V/Sc multilayer annealed at 250˚C.

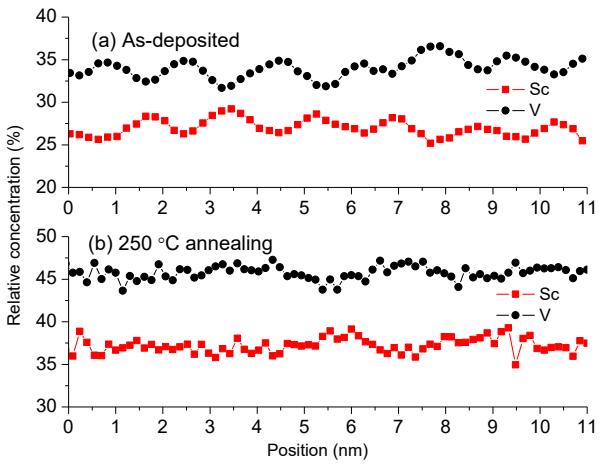

Fig.5. EDX line scan of (a) the as-deposited 400-bilayer sample, and (b) the 100-bilayer sample after annealing at 250°C. (perhaps you should indicate to which location corresponds the zero value. Is it the surface?)

3.2 Temporal stability

The GIXR measurements of the V/Sc multilayer with 400 bilayers stored for 2 ~~months~~, 4 ~~months,~~ and 6 months are depicted as Fig. 6. The as-deposited result is also shown as a comparison. It can be found that the reflectance of the1st and 2nd order Bragg peaks of the sample stored after different times are essentially the same and the d-spacing remains as 1.59 nm. It means that the main part of the periodic layer structure were unchanged after 6 months storage. The oscillation of the reflectance curve at about 1º~2° was slightly shifted to the lower angle with time which indicates a gradual change of the surface B_4C layer and possibly of the first few V/Sc bilayers ~~of V and Sc~~. Similar phenomenon was also observed in other multilayer mirrors after a long time storage [19].

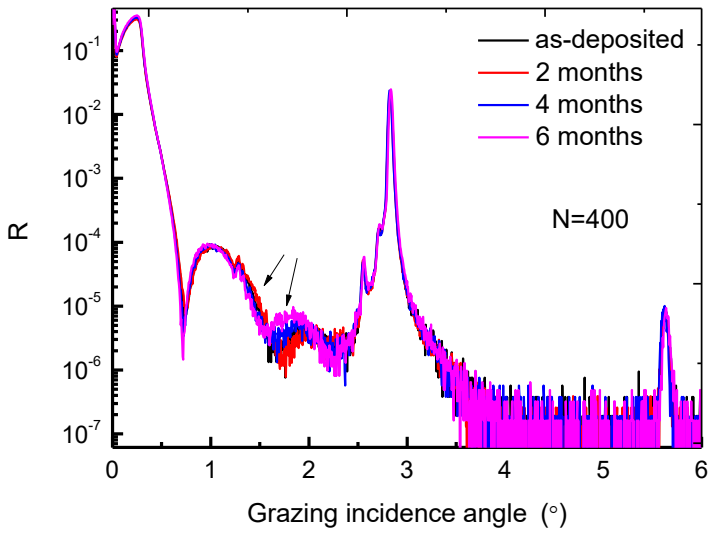

Fig. 6. Temporal evolution of GIXR in a half year for the V/Sc multilayer with 400 bilayers.

The SXR reflectance of the V/Sc sample with 400 bilayers was measured again at the BEAR beamline after a storage of 6 months and the result is displayed in Fig. 7. The reflectance curve of the as-deposited sample is also shown as a comparison. They were both measured under a near normal incidence of 9˚. The peak reflectance dropped slightly from 18.4% to 16.5% at 3.128 nm. Considering that the aged sample was measured with a beam of higher energy resolution than the as-deposited one, 0.2 eV instead of 0.4 eV, there should be another ~0.6% drop of reflectivity of the aged sample (according to

simulation), if using the same incidence beam. This also contributes to the narrower bandwidth of the aged sample. The reduction of the SXR reflectivity can originate from the surface oxidation and other chemical changes mostly in the surface structure after exposure to air for a long time [7,20]. Despite the minor reflectance decrease, the temporal stability of the V/Sc multilayer is relatively good for using as optical elements in X-ray microscopy applications.

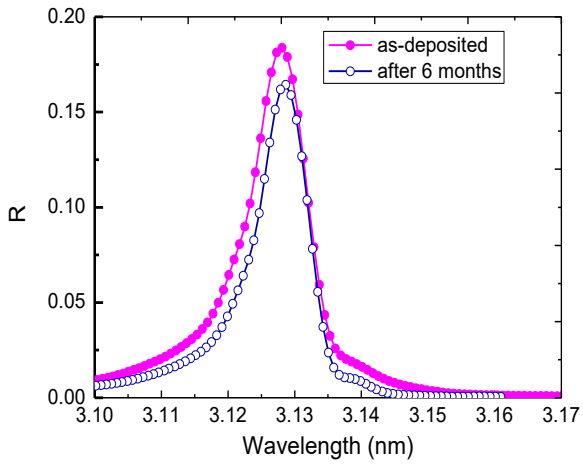

Fig. 7. SXR curves of the 400-bilayer V/Sc multilayer as-deposited and after six months storage.

3 Conclusions

V/Sc multilayer is a very promising candidate for high reflectivity mirror ~~used~~ in the water window region. To study its thermal and temporal stabilities, the structure evolution and the optical performance change of the multilayer under different temperatures annealing and a long-term storage were investigated. It is found from the GIXR and SXR measurements that the layer structure and the ~~SXR~~ reflectivity of V/Sc remain almost unchanged after 100˚C annealing. The SXR reflectivity deteriorates obviously after annealing at 200˚C, and the reflectivity drops almost to zero at 250˚C. According to the XRD and TEM measurements, a severe crystallization of V and Sc was found with randomly distributed nano-grains after 250˚C annealing. This was accompanied by an elemental mixture at the interfaces and these two processes ruined the ultra-thin layer structure. The multilayer was relative stable after 6 months storage in air with only ~2.5% decrease of the SXR reflectivity (absolutely). Although the V/Sc multilayer exhibits a little worse thermal stability than the widely used Cr/Sc multilayer, different interface engineering methods can be explored to improve it. Adding interface barrier layers or nitridation of the multilayer have both been demonstrated effective on enhancing the thermal stability [7,16].This can be further investigated in the future experiments.

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